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Relaxation and Nanocrystal Formation in Vanadium Tellurite Glasses

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Recently we discovered that nanocrystals formed in vanadium tellurite (VT) glass anodes for lithium ion batteries upon Li-ion discharging/charging, and thereby the battery cycling stability was greatly enhanced. This kind of nanocrystal formation has a fundamentally different origin compared to the thermally induced crystallization. This discovery motivates us to do detailed studies in order to understand the origin of the ion-insertion induced nanocrystal formation in VT glasses. To do so, we study a series of VT glasses with various V₂O₅/TeO₂ ratios regarding their enthalpy relaxation, structural heterogeneity and nucleation by differential scanning calorimetry and structural analysis. Our DSC results show that the VT systems are poor glass formers with high fragility ($m \approx 80-100$). We find that high degree of structural and energetic heterogeneities exist in those glasses, and high potential energy domains are the precursors for nanocrystal formation. Through Li-insertion, the higher energy domains tend to be transformed into ordered domains, nanocrystals with lower potential energy, and simultaneously some of inserted Li ions join the lattice structure. Finally, we propose a possible microscopic picture of the disorder-order transition in TV glasses, and describe the compositional conditions under which such transition can occur.